

**LIBRARY - AIR RESOURCES BOARD**

FINAL REPORT

SOUTHERN CALIFORNIA AIR QUALITY STUDY

Part I. Hydrocarbon Collection and Analyses

Part II. Air Toxics Collection and Analyses

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## CONTENTS

### I. SCAQS: Hydrocarbon Measurements

1.	Executive Summary	1
2.	Air Sample Collection Method	3
3.	Hydrocarbon Analysis Methods	4
4.	Conditions of Analysis	5
	Data Set 1 Hydrocarbon Speciation	
	Data Set 2 C <sub>2</sub> -C <sub>4</sub> Hydrocarbons	
	Data Set 3 CO and CH <sub>4</sub>	

### II. TACS: Air Toxics Contaminant Study

1.	Executive Summary	10
2.	Air Sample Collection method	11
3.	Air Toxics Analysis Method	11
4.	Condition of Analysis	12
5.	Calibration	12
	Data Set 4 Air Toxics	

## Part I. SCAQS: Hydrocarbon Measurements

## 1. SUMMARY

Task A

This task required that 600 stainless steel sampling containers be available to the field work. In actuality, 735 canisters were sent to AeroVironment, Inc.; 695 were filled and analyzed by EPA and/or OGC (see Table 1). In addition, 40 canisters were returned unused via AeroVironment, Inc., at the end of the project.

All of the ground-air sampling stations operated satisfactorily, collecting one-hour integrated samples. The systems used for the winter sampling period were modified to use two pumps. This change eliminated the potential early morning problem of high humidity condensate forming in the flow controller orifices. The problem was experienced intermittently at two of the summer stations.

The aircraft systems (2) worked properly for filling the 3.2-L canisters to 20 psig over a 5-minute period at a constant flow rate.

Training ARB-designated personnel through AeroVironment, Inc., worked out very satisfactorily.

Task B

Hydrocarbon analyses for QA on 10% of the 600 samples analyzed by EPA were performed. The results for these 60 samples were submitted to ARB. The data are included in this report as Data Set 1.

In addition, three samples from the Downtown Los Angeles set were analyzed twice to determine the reproducibility of the measurements. The agreement between the paired analyses was typically less than  $\pm 2\%$ .

Inter-calibration between EPA and OGC was accomplished through the multiple exchange of three different ambient air samples. The air samples were prepared from cryogenic transfers of Los Angeles air stored in 15-L tanks. The source samples were stored at high pressure,  $>150$  psig, in special SS tanks, and aliquots at 60 psig were taken from these tanks to fill the 6-L bottles exchanged in the round-robin inter-calibration. The data were submitted to ARB, and Eric Fujita prepared an in-depth report analyzing the agreement, biases, and linearity of the respective participants (J.

Collins and E. Fujita, Quality Assurance for the Southern California Air Quality Study, Final Report. ARB Contract A6-122-32, California Air Resources Board, Sacramento, 1989). The overall conclusion was that the agreement among the four laboratories that participated in the study (Environmental Protection Agency-L. Stockberger, Washington State University-H. Westberg, Environmental Protection Agency-W. Lonneman, Oregon Graduate Center-R.A. Rasmussen) was very good,  $\pm 10\%$ .

Separately we compared the stabilities of the aromatic hydrocarbons (benzene, toluene, ethylbenzene, and the xylenes) between the source tanks and the samples over the seven-month period that the inter-calibration exchange took place. A comparison of the differences between the assigned values in the source tanks and the monthly means determined from the analysis made on the samples upon their return to OGC before they were sent out again for inter-calibration was conducted. A total of six different analyses were made on the samples over the seven-month period. The summary data are given in Table 2 and plotted in Figure 1. The data show no drift in the samples and very small differences between the assigned value and the measured value, typically  $< \pm 5\%$ .

The QA of the calibration of the working standard (neohexane @ 0.226 ppmv) used during the study is shown in Table 3. Two NBS-SRM primary standards, propane at 2.87 ppmv and benzene at 0.254 ppmv, have been used periodically to determine the absolute value of neohexane and to measure any drift in the neohexane standard. We have used neohexane as our daily working standard for fourteen years. It is one of the few hydrocarbons that can be used as an internal standard in urban air samples.

The data reported to ARB are organized as follows:

#### Data Set 1

##### Hydrocarbon Speciation ( $C_2$ - $C_{10}$ )

Anaheim	17 samples
Burbank	3 samples
Hawthorne	3 samples
Long Beach	20 samples
Downtown Los Angeles	15 samples
Rubidoux	<u>3</u> samples
	61

Replicate Analyses  
Downtown Los Angeles                      3 samples

#### Data Set 2

Light Hydrocarbons ( $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ ,  $C_3H_8$ ,  $C_3H_6$ ,  $i-C_4H_{10}$ , and  $n-C_4H_{10}$ )  
Summer 19 June - 3 September 1987 at Anaheim (32), Azuza (32),  
Burbank (31), Claremont (60), Downtown Los Angeles (32),  
Hawthorne (30), Long Beach (65), Rubidoux (35), and San Nicolas  
Island (29). Total: 346 samples analyzed.

Winter 11 November - 11 December 1987 at Anaheim (9), Burbank  
(16), Downtown Los Angeles (20), Hawthorne (16), Long Beach (12),  
and Rubidoux (16). Total: 89 samples analyzed.

#### Data Set 3

CO and  $CH_4$  Results for Summer and Winter Samples

Summer 19 June - 3 September 1987 at Anaheim (33), Azuza (33),  
Burbank (33), Downtown Los Angeles (33), Claremont (66),  
Hawthorne (33), Long Beach (66), Rubidoux (33), San Nicolas  
Island (33). Total: 363 samples analyzed.

Winter 11 November - 11 December 1987 at Anaheim (17), Burbank  
(18), Downtown Los Angeles (36), Hawthorne (18), Long Beach (34),  
and Rubidoux (18). Total: 141 samples analyzed.

## 2. AIR SAMPLE COLLECTION METHOD

Stainless steel (type 304) cans internally electropolished by the SUMMA<sup>R</sup> process were used to provide state-of-the-art collection-storage of ambient air samples for quantitative hydrocarbon analyses at trace levels. The bottles (6-L) were sent into the field under high vacuum (<100 mTorr) and were fitted with non-contaminating bellows stem (Nupro SS-4H4) high vacuum valves and Cajon<sup>R</sup> VCR vacuum coupling fittings. One-hour integrated samples were collected. Individual samplers were used to collect for the specified periods: 0700, 1200, and 1600 hours at all sites, and 0500, 1400, and 1800

at Claremont and Long Beach. The sample periods were prescribed by the experiment. The sample lines were flushed with outside air via a purge-tee gauge assembly to eliminate any contamination obtained from storage indoors in the sample connection lines (dead volume 10 mL) before initiating the sampling. The vacuum in the tanks was checked with a Span<sup>R</sup> gauge (-30 to +30) and the system left in the ready-to-sample position. A Chrontrol<sup>R</sup> 4CD-115VAC timer was used to activate the sampling start-stop sequence. Non-contaminating back pressure regulators, solenoids, Teflon<sup>R</sup>-faced diaphragm FC-1121 pumps, and upstream sample dump-crosses were used to provide a contaminant-free, constant rate of sampling at 100 mL/min. Terminal pressures in the flasks were pre-set to be 12 psig  $\pm$  2 psig.

### 3. HYDROCARBON ANALYSIS METHODS

The samples were analyzed for CH<sub>4</sub>, CO, and C<sub>2</sub>-C<sub>10</sub> hydrocarbons. The standard operating procedure used to speciate the C<sub>1</sub>-C<sub>10</sub> hydrocarbons was to use several different gas chromatographs with species-specific and/or very sensitive detectors. Each instrument was dedicated to a specific group of compounds. The procedure for handling the sample analysis sequence was:

- (A) Upon receipt of the samples, logged in the sample container serial number, date, time, and place. Assigned a sample number to each sample.
- (B) Measured the pressure in the can. This was verified against the pressure recorded in the field.
- (C) First analysis was for CH<sub>4</sub>, CO, and CO<sub>2</sub> via a Carle 211M-S gas chromatograph. This analysis established the general background pollutant level of the samples.
- (D) Second analysis was for C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, i-C<sub>4</sub>H<sub>10</sub>, and n-C<sub>4</sub>H<sub>10</sub> via a PE 3920-B or an HP 5890-A GC system.
- (E) Third analysis was for the C<sub>3</sub> to C<sub>10</sub> hydrocarbons using a cryo-focused sample on a capillary column and a temperature-programmed method. This analysis provided the needed hydrocarbon speciation for C<sub>3</sub>-C<sub>10</sub> compounds.

#### 4. CONDITIONS OF ANALYSIS

CH<sub>4</sub>, CO, CO<sub>2</sub>

A Carle<sup>R</sup> 211M-S gas chromatograph with a Hewlett-Packard 3388 data processor was used to measure CH<sub>4</sub>, CO, and CO<sub>2</sub>. The columns arranged in a back-flush were silica-gel 8-ft. x 1/8-inch and Mol-sieve 5Å 3-1/2-ft. x 1/8-inch; oven temperature, 76°C; sample size, 3 mL. The Ni-catalyst was thermostatted at 400°C. Total analysis time was 8 minutes. Precision of analysis for CH<sub>4</sub> at 1600 ppbv is 0.2 to 0.3%; CO at 100 ppbv, ±5%; and CO<sub>2</sub> at 350 ppmv, ±0.4%. The response for CH<sub>4</sub> and CO was linear from 20 ppbv to 20,000 ppbv.

C<sub>2</sub> to C<sub>4</sub> Hydrocarbons

An HP 5890-A GC system with a pair of HP 3390 integrators was used for these analyses. A matched pair of phenyl isocyanate/Durapak<sup>R</sup> 15-ft. x 1/8-inch columns were used. The oven temperature was 40°C, sample size 250 mL, and analysis time 8 minutes. After each analysis, the column was cooked out for 15 minutes at 55°C. Detection limit for the C<sub>2</sub>-C<sub>4</sub> species was ~40 pptv. Precision of analysis was typically better than ±2% at 1 ppbC levels.

C<sub>3</sub>-C<sub>10</sub> Hydrocarbons

An HP 5790A GC system with a pair of HP 3393 data processors was used to integrate the C<sub>3</sub>-H<sub>10</sub> hydrocarbons. A pair of wide bore (1 mm) glass capillary columns (DB-1) with 0.25μ film thickness and 30-m lengths were used. The oven temperature was programmed from -70° to 150°C at 8°/min. after an initial 2-minute hold. Sample volume was 500 mL enriched via an 8-inch x 1/8-inch U-trap immersed in liquid oxygen and released at +80°C (hot water) where the hydrocarbons were subsequently cryo-focused on the head of the column at -70°C.

Table 1  
Stainless Steel Canisters Used in SCAQS

Ground Samples

Location	Summer	Winter	
Anaheim	33	18	
Azuza	39		
Burbank	34	18	
Claremont	66		
Downtown Los Angeles	46	36	
Hawthorne	34	18	
Long Beach	71	36	
Rubidoux	33	19	
San Nicolas Island	<u>34</u>	<u>      </u>	
Sub-Total	390	145	590

Aircraft Samples

University of Washington	36	0	
STI	<u>20</u>	<u>49</u>	
Sub-Total	56	49	<u>105</u>
Sub-Total - Used			695
Sub-Total - Returned Unused			<u>40</u>

TOTAL CANISTERS DEPLOYED 735



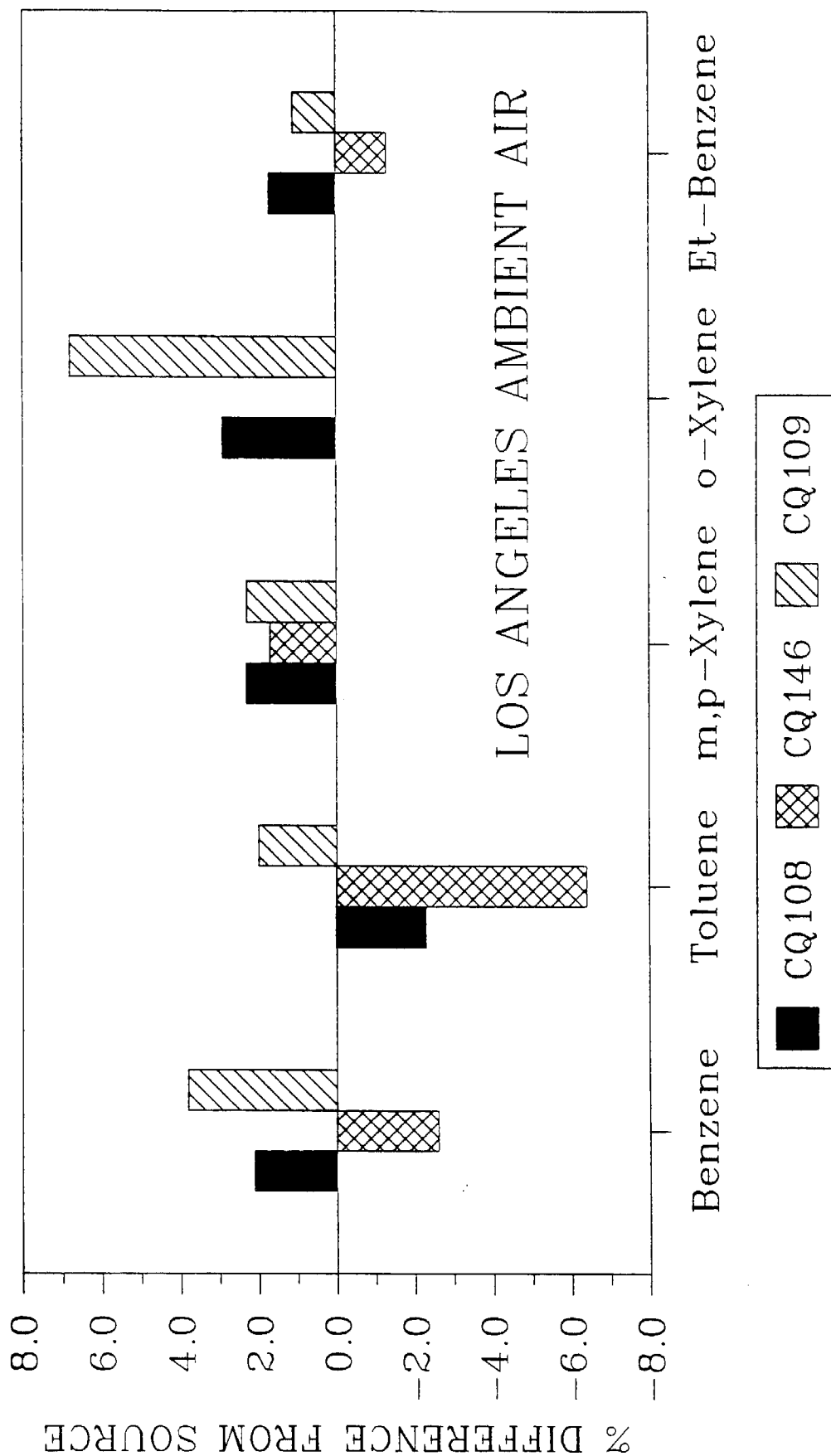
Table 2  
Long-Term Ambient Air Samples Hydrocarbon Stability  
Comparison of Sample-Source Means

		Benzene	Toluene	Ethyl- Benzene	p/m-Xylene	o-Xylene
I.	Source WM43					
	$\mu\text{g}/\text{m}^3$	$x_{(3)}$	9.4	26.2	4.3	14.9
	5.8					
	$\pm$	0.6	0.6	0.2	0.3	0.2
	%	6	2.2	3.8	2.1	3.6
	Sample CQ108					
	$\mu\text{g}/\text{m}^3$	$x_{(7)}$	9.6	25.6	15.7	5.9
	$\pm$	0.3	1.1	0.3	1.1	0.3
	%	2.8	4.2	7.5	6.8	4.7
	Difference					
	Sample-					
	Source					
	$\mu\text{g}/\text{m}^3$	+0.2	0.6	+0.1	0.8	0.1
	%	+2.1	-2.3	+2.3	+2.9	+1.7
II.	Source WM9					
	$\mu\text{g}/\text{m}^3$	$x_{(3)}$	11.4	34.6	20.8	7.6
	$\pm$	0.2	0.8	0.4	0.6	0.3
	%	2	2.4	6.4	3.1	3.5
	Sample CQ146					
	$\mu\text{g}/\text{m}^3$	$x_{(7)}$	11.1	32.4	20.9	7.5
	$\pm$	0.4	2.3	0.4	1.4	0.5
	%	3	7.1	6.7	6.9	6.9
	Difference					
	Sample-					
	Source					
	$\mu\text{g}/\text{m}^3$	0.3	2.2	0.1	0.1	0.1
	%	-2.6	-6.4	+1.7	<0.01	-1.3
III.	Source CQ145					
	$\mu\text{g}/\text{m}^3$	$x_{(3)}$	2.6	87.8	52.7	18.9
	$\pm$	0.1	2.1	3.8	14.5	1.8
	%	3.8	2.4	7.1	9.8	9.5
	Sample CQ109					
	$\mu\text{g}/\text{m}^3$	$x_{(7)}$	2.7	89.6	53.9	19.1
	$\pm$	0.1	3.6	5.0	14.6	2.2
	%	2.1	4.1	9.3	9.4	11.5
	Difference					
	Sample-					
	Source					
	$\mu\text{g}/\text{m}^3$	0.1	1.8	1.2	3.6	0.2
	%	+3.8	+2.0	+2.3	+6.8	+1.1

\*Data used to generate Figure 1

Figure 1

# STABILITY OF AROMATIC HYDROCARBONS IN INTERNALLY ELECTROPOLISHED 6L SS CANISTERS TIME 7 MONTHS



CALIBRATED VS. NBS SRM # 1805 BENZENE IN N2

Table 3  
Long-Term QC Primary Standard

QUALITY CONTROL ANALYSIS: CALIBRATION STABILITY  
PERIODIC CERTIFICATION OF DAILY WORKING STANDARD

<u>Primary Standards</u>	<u>Given Value</u>	<u>Analysis</u>	<u>Neohexane Working Standard</u>		<u>Percent</u>
	<u>ppmv</u>	<u>Date</u>	<u>Assigned</u>	<u>Measured</u>	<u>Difference</u>
			<u>ppmv</u>	<u>ppmv</u>	
Benzene NBS-SRM #1805 CAL 5679	0.254	Dec. 1985	0.226	0.224	-2%
Benzene NBS-SRM #1805 CAL 5679	0.254	June 1987	0.226	0.233	+4%
Benzene NBS-SRM #1805 CAL5679	0.254	Nov. 1987	0.226	0.219	-3%
Benzene NBS-SRM #1805 CAL5679	0.254	Apr. 1988	0.226	0.221	-3%
Propane NBS-SRM #1665-B FF27623	2.87	Mar. 1988	0.226	0.218	-4%
Benzene NBS-SRM #1805 CAL5679	0.254	Oct. 1988	0.226	0.222	±2%
Propane NBS-SRM #1665B FF27623	2.87	Oct. 1988	0.226	0.224	±1%
Benzene NBS-SRM #1805 CAL5679	0.254	June 1989	0.226	0.205*	-9%
Propane NBS-SRM #1665B FF27623	2.87	June 1989	0.226	0.225	±1%

\* Measured Neohexane values determined against NBS-SRM standards. Benzene NBS-SRM is possibly drifting downward. Neohexane, calibrated against the Propane NBS-SRM, is in excellent agreement with the assigned value. When the NBS-SRM Benzene tank is referenced against the Propane and/or the Neohexane standards, it typically was measured to be 10% low.

## Part II. TACS: Air Toxics Contaminant Study

1. SUMMARYTask A

This task required that 64 stainless steel sampling tanks of 15-L be filled and analyzed for 13 compounds. The tanks were internally electropolished type 304 SS and equipped with Nupro SS-4H4 valves. The tanks were evacuated to 60 mT and Helium leak-tested to  $10^{-9}$  scc/min prior to shipment.

Four samplers were provided to AeroVironment, Inc., that were programmed to collect integrated air samples at a constant flow rate (21 mL/min) over 24 hours. The four sites were Claremont, Downtown LA, Long Beach, and Rubidoux, which were co-located with the SCAQS hydrocarbon speciation studies. The four systems worked properly during both the summer and the winter sampling periods.

Training ARB-designated personnel through AeroVironment, Inc., worked out very satisfactorily.

Task B

Analysis of the designated air toxics (Table 4) was performed on 56 of the 64 samples. Five of the samples were voided in the field because of operational problems. The results for the 56 samples were submitted to ARB. The data are included in this report as Data Set 4. The data reported are organized in Data Set 4 as follow:

	Summer	Winter
Claremont	11	0 samples
Downtown LA	12	5 samples
voided	3	
Long Beach	11	7 samples
voided	1	
Rubidoux	10	0 samples
voided	<u>1</u>	<u>      </u>
	44	12 samples

## 2. AIR SAMPLE COLLECTION METHOD

The approach used was essentially the same as that used for the hydrocarbon studies in Section I, 2. The size of the sampling canisters was increased from 6 to 15 L and the flow rate reduced from 100 to 21 mL/min. The units were turned on and off manually, which eliminated the need for a Chrontrol<sup>R</sup> timer and solenoids. The final pressures in the tanks after 24 hours were typically  $10 \pm 3$  psig.

## 3. AIR TOXICS ANALYSIS METHODS

The samples were analyzed for 13 compounds as given in the list in Table 4. The approach was to measure benzene, m,p-xylene, o-xylene, and chlorobenzene with a GC-FID system using capillary columns. The lower detection limit for these hydrocarbons is 0.2 ppbv/compound. The remaining compounds were measured using a capillary column in a GC-ECD instrument. The procedure for handling the sample analysis sequence was:

- (A) Upon receipt of the samples, logged in the sample container serial number, date, time, and place. Assigned a sample number to each sample.
- (B) Measured the pressure in the can. This was verified against the pressure recorded in the field.
- (C) First analysis was for  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{CO}_2$  via a Carle 211M-S gas chromatograph. This analysis established the general background pollutant level of the samples.
- (D) Second analysis was for  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_3\text{H}_6$ , i- $\text{C}_4\text{H}_{10}$ , and n- $\text{C}_4\text{H}_{10}$  via a PE 3920-B or an HP 5890-A GC system.
- (E) Third analysis was for the  $\text{C}_3$  to  $\text{C}_{10}$  hydrocarbons using a cryo-focused sample on a capillary column and a temperature-programmed method. This analysis provided the needed hydrocarbon speciation for benzene, chlorobenzene, and the xylenes.
- (F) Fourth analysis was for the seven chlorinated hydrocarbons and the two brominated species. The method used a cryo-focused sample on a capillary column and a temperature-programmed operation in a GC-ECD instrument.

#### 4. CONDITION OF ANALYSIS

The CO and the benzene, xylenes, and chlorobenzene conditions of analysis are the same as reported in Section I, 4.

The GC-ECD conditions of analysis were a PE 3920B instrument with  $^{63}\text{Ni}$  ECD and an HP 3388 integrator. The capillary column was a DB-1 60 m x 0.32 mm x 1.0  $\mu\text{m}$  film thickness. The oven temperature was programmed from  $-73^\circ\text{C}$  (2-minute hold) at  $8^\circ\text{C}/\text{min}$  to  $150^\circ\text{C}$ . The ECD was operated at  $200^\circ\text{C}$ . The carrier gas was He at 1 mL/min with Ar (95%)/CH<sub>4</sub>(5%) make-up gas. Sample size was 25 mL trapped at liquid O<sub>2</sub> temperature ( $-183^\circ\text{C}$ ) on a glass bead trap prior to injection for on-column cryo-focusing.

#### 5. CALIBRATION

During the course of this study, 1987-79, a new calibration standard with 13 compounds (single tank) was prepared at the 5 to 10 ppbv level for the specified compounds required for this Air Toxics study. This standard was believed to be more accurate than the earlier standards available in several tanks at the less than 1 ppbv level used in 1987 and early 1988 analyses. In addition, the ECD-GC system was studied to develop a method that had a more linear response to halogenated hydrocarbons in the expected urban range of concentrations from 0.5 to 10 ppbv. A test chromatogram of the new calibration standard is given in Figure 2.

The electron capture detector exhibits a wide range of response per nanogram for each compound shown in Table 5. The response is dependent upon a variety of factors. As shown in Table 5, only the relative response to different make-up gases is reported. The greatly increased sensitivity of weakly adsorbing species obtained with the use of O<sub>2</sub>-doping of the detector has been used in my laboratory for years. This approach is necessary in order to measure the trace pptv levels of certain halocarbons in clean background air. However, it introduces a severe non-linearity problem when the higher concentrations observed in urban air are measured. Therefore, we undertook a study to determine the effect of three different make-up gases on the linearity of the ECD: O<sub>2</sub>(0.14%)/N<sub>2</sub>, pure N<sub>2</sub>, and Ar(95%)/CH<sub>4</sub>. O<sub>2</sub>-doped N<sub>2</sub> make-up gas enhances the response of the electron capture detector to weakly absorbing compounds so that they can be measured in background air

samples at low pptv levels.  $O_2$ -doped  $N_2$  has been used successfully in the ECD-GC determination of background  $CH_3Cl$  and organo-bromine compounds such as  $CH_3Br$ ,  $CH_3-CH_2Br$ , and  $CH_2BrCl$ . It is the system of choice for measuring weakly absorbing compounds. The linearity of the ECD response to the 11 compounds listed in Table 5 was first tested using  $O_2(0.14\%)/N_2$  as the make-up gas. Pure  $N_2$  was tried as the second make-up gas. In previous studies when analyzing background air samples, it gave higher responses to  $CH_3Br$ ,  $CH_2Cl_2$ ,  $CHCl_3$ , and  $CH_2Cl-CH_2Cl$  (EDC) than  $Ar(95\%)/CH_4$ .  $Ar(95\%)/CH_4$  was the third make-up gas studied and gave the best linearity in response when analyzing the range of <1 to 10 ppbv levels of the compounds.

The concentration range over which the ECD was linear for the  $Ar(95\%)/CH_4$  make-up gas used is given in Table 6. Also included is the precision of the analyses. Under these conditions the detection limit for  $CH_2Cl_2$  and  $CH_2Cl-CH_2Cl$  (EDC) was 0.2 ppbv, and for the other seven toxic air contaminants the lower limit was 0.05 ppbv. The conditions with the  $Ar(95\%)/CH_4$  make-up gas do not provide the extreme sensitivity needed for trace level measurements but appear better suited to the concentrations expected in urban air samples. The original ECD-GC system employed in 1987 and early 1988 used an  $O_2(0.14\%)N_2$  make-up gas. While ideally suited to measuring trace levels of weakly absorbing species, it is not useful for measuring highly absorbing species such as  $CCl_3F$  (F-11),  $CH_3CCl_3$ ,  $CCl_4$ , and  $CCl_2=CCl_2$  (PCE) that tend to saturate the ECD even at low ppbv concentrations. The  $O_2$ -doped system we used was best operated for analyzing low pptv levels of the weakly absorbing compounds in clean air. In these types of measurements a wide linear range is not needed; rather, a very narrow range of concentrations is measured with high precision, <1%. The standards used and the samples analyzed usually have similar concentrations. For example, when analyzing clean background air samples, a calibrated tank of ambient air is used as the standard.

Plots of the linearity for several selected compounds ( $CHCl_3$ ,  $CH_3Br$ , EDB,  $CH_3CCl_3$ ,  $CCl_4$ , F-11, and PCE) are given in Figure 3-9. As expected, non-linearity at the higher concentrations is observed for the strongly electron-absorbing species  $CCl_4$ , F-11, and PCE, even with the addition of the highly moderating effect of the  $Ar(95\%)/CH_4$  make-up gas.

There are sufficient amounts of both the primary new standard at 5 to 10 ppbv and the diluted working standard of 0.5 to 1 ppbv to exchange with ARB or other interested laboratories. I expect that we will maintain a QA study on this standard for the next several years.



Table 4  
Air Toxics Species List

Name	Abbreviation Used in Data Tables	Limit of Detection (ppbv)
1. ethylene dibromide	EDB	0.3
2. ethylene dichloride	EDC	0.6
3. benzene	Bz	0.1
4. carbon tetrachloride	$\text{CCl}_4$	0.1
5. methylene chloride	$\text{CH}_2\text{Cl}_2$	0.5
6. trichloroethylene	$\text{C}_2\text{HCl}_3$	0.1
7. perchloroethylene	$\text{C}_2\text{Cl}_2$	0.1
8. chloroform	$\text{CHCl}_3$	0.1
9. methyl bromide	$\text{CH}_3\text{Br}$	0.3
10. methyl chloroform	$\text{CH}_3\text{CCl}_3$	0.1
11. chlorobenzene	Cl-Bz	0.2
12. xylene (m-p)	X-m,p	0.1
13. xylene (o)	X-o	0.1

Table 5

Relative response per nanogram of compound with different make-up gases

Compound	Ar(95%) CH <sub>4</sub>	N <sub>2</sub>	O <sub>2</sub> (0.14%) DOPED N <sub>2</sub>
CH <sub>3</sub> Br	1006	3795	16042
CCl <sub>3</sub> F (F-11)	142676	142526	132309
CH <sub>2</sub> Cl <sub>2</sub>	259	952	11530
CHCl <sub>3</sub>	12131	19828	23652
CH <sub>2</sub> Cl-CH <sub>2</sub> Cl (EDC)	185	785	13317
CH <sub>3</sub> -CCl <sub>3</sub>	37493	49398	50881
CCl <sub>4</sub>	118339	63794	58289
CH <sub>3</sub> -CHCl-CH <sub>2</sub> Cl (DCP)	152	573	12830
CHCl=CCl <sub>2</sub> (TCE)	14323	22711	23342
CH <sub>2</sub> Br-CH <sub>2</sub> Br (EDB)	16582	24209	26340
CCl <sub>2</sub> =CCl <sub>2</sub> (PCE)	54170	63542	56075

Table 6

Concentration in standard, precision of analysis and linear range for each compound for the system with Ar(95%)/CH<sub>4</sub> as the make-up gas to detector.

Compound	Concentration		Precision of anal.	Linear range
	(ppbv)	(ug/m <sup>3</sup> )		
CH <sub>3</sub> Br	4.96	19.27	2.2%	0.5-40.0
CCl <sub>3</sub> F (F-11)	5.26	29.58	1.2%	0.5-40.0
CH <sub>2</sub> Cl <sub>2</sub>	10.80	37.55	3.4%	1.0-80.0
CHCl <sub>3</sub>	10.60	51.81	2.1%	0.5-50.0
CH <sub>2</sub> Cl-CH <sub>2</sub> Cl (EDC)	9.90	40.09	4.3%	1.0-80.0
CH <sub>3</sub> -CCl <sub>3</sub>	5.12	27.96	2.3%	0.5-40.0
CCl <sub>4</sub>	9.94	62.61	2.4%	0.5-40.0
CH <sub>3</sub> -CHCl-CH <sub>2</sub> Cl (DCP)	5.40	24.96	6.5%	5.0-40.0
CHCl=CCl <sub>2</sub> (TCE)	10.80	58.09	4.4%	0.5-80.0
CH <sub>2</sub> Br-CH <sub>2</sub> Br (EDB)	5.50	42.29	6.4%	0.5-40.0
CCl <sub>2</sub> =CCl <sub>2</sub> (PCE)	10.50	71.29	4.6%	0.5-80.0

Figure 2

NEW TOXICS (HALOCARBON) STANDARD

2"

New calibration standard

prepared in 1988.

Working range 0.5 to 1 ppbv

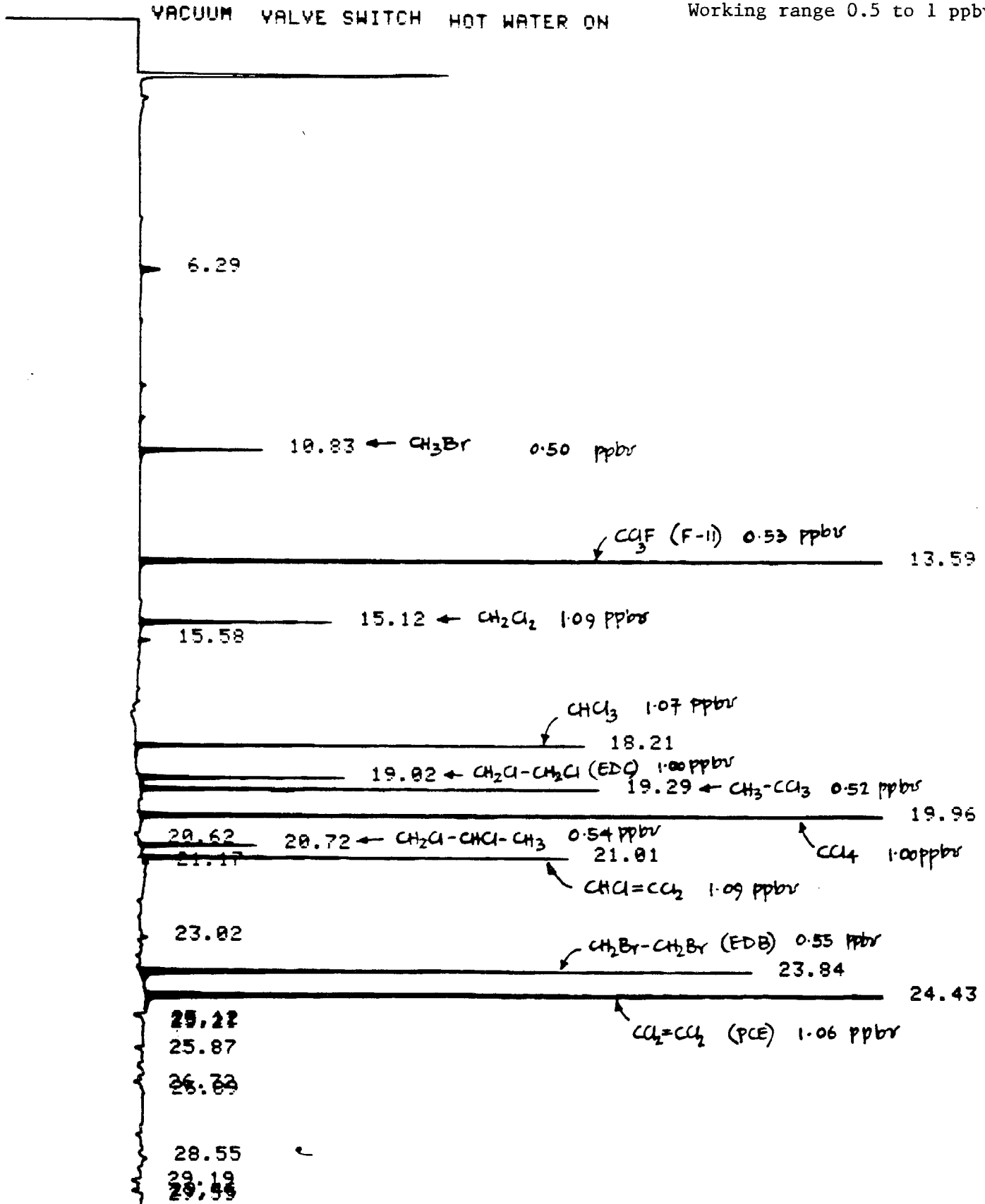


Figure 3

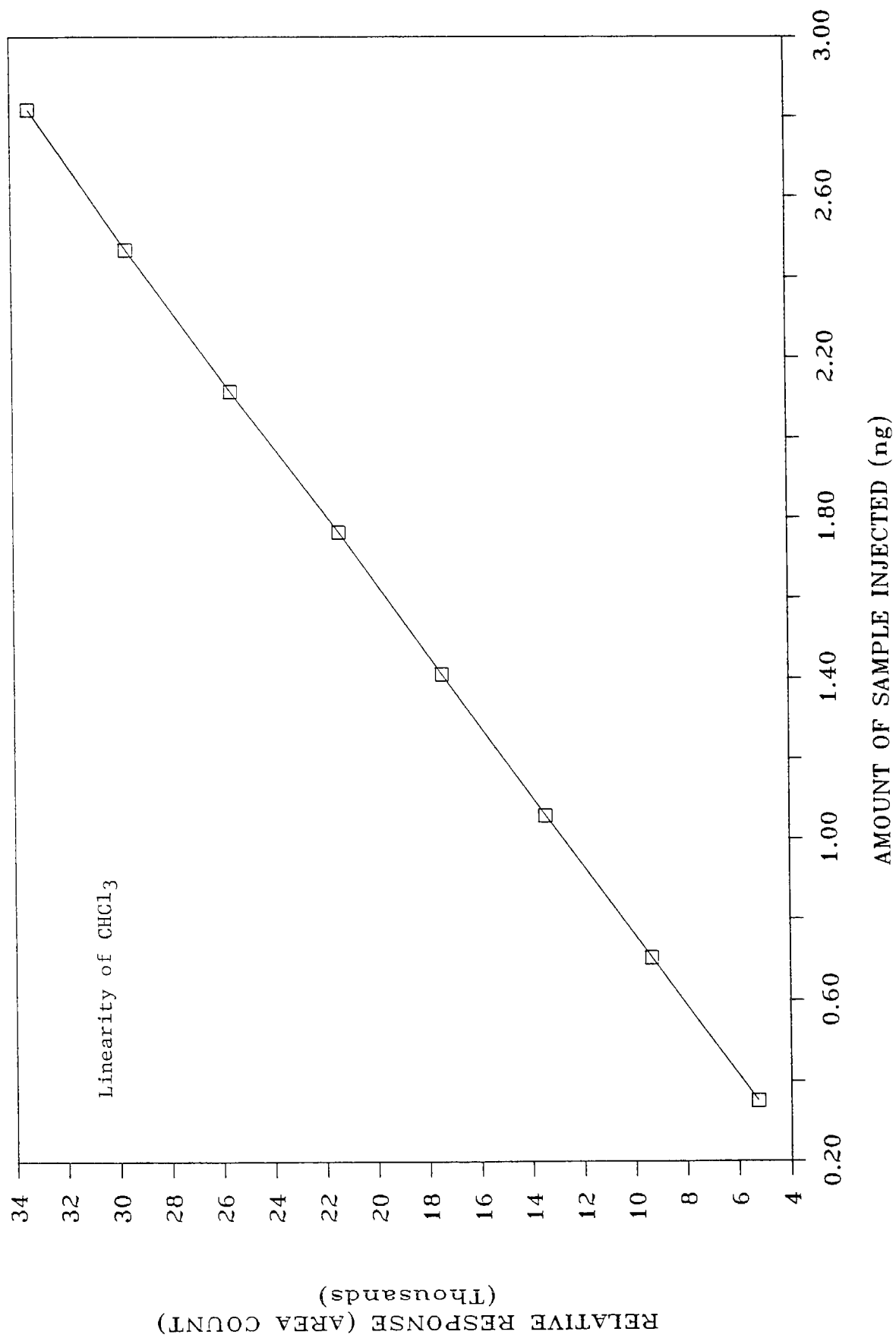


Figure 4

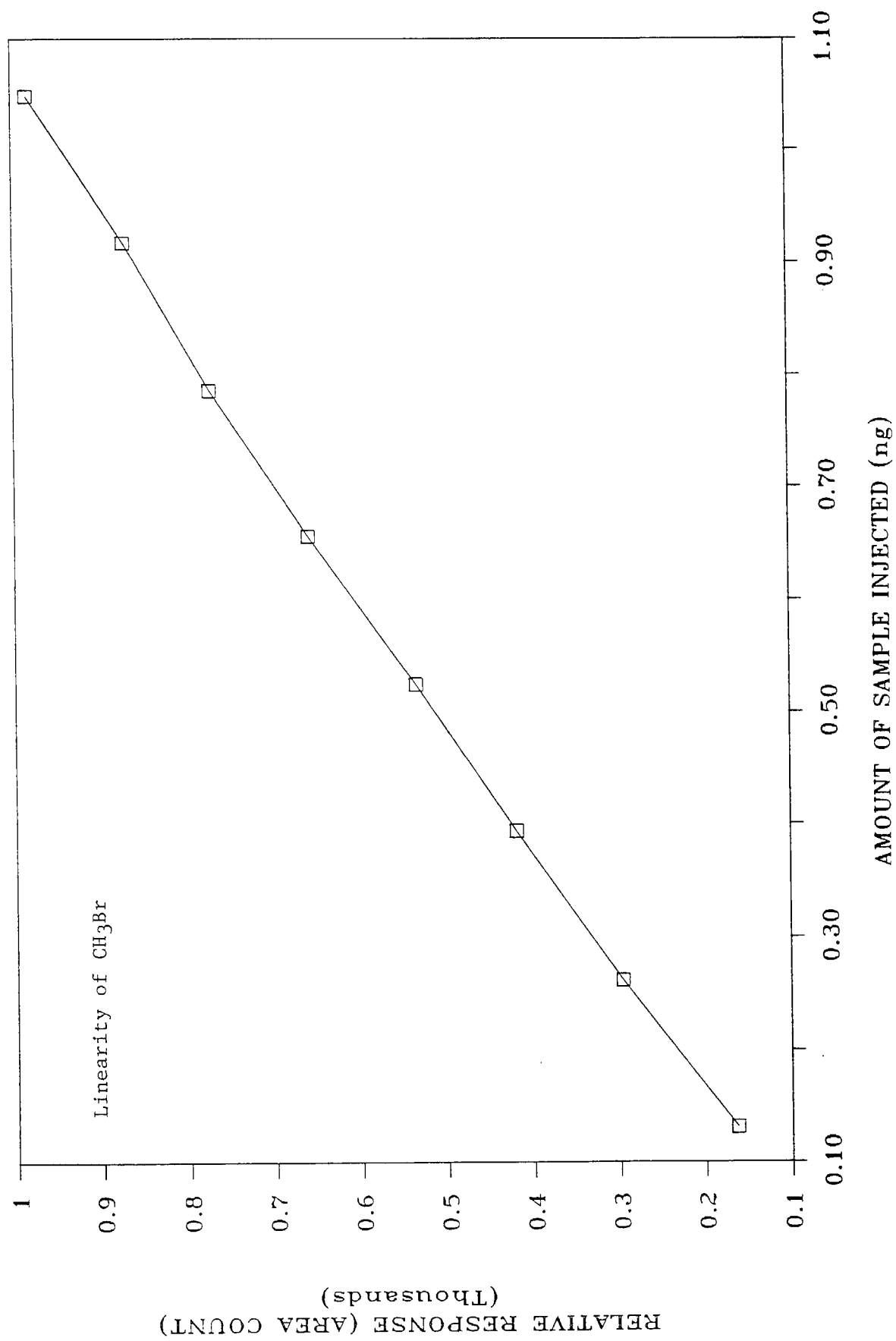


Figure 5

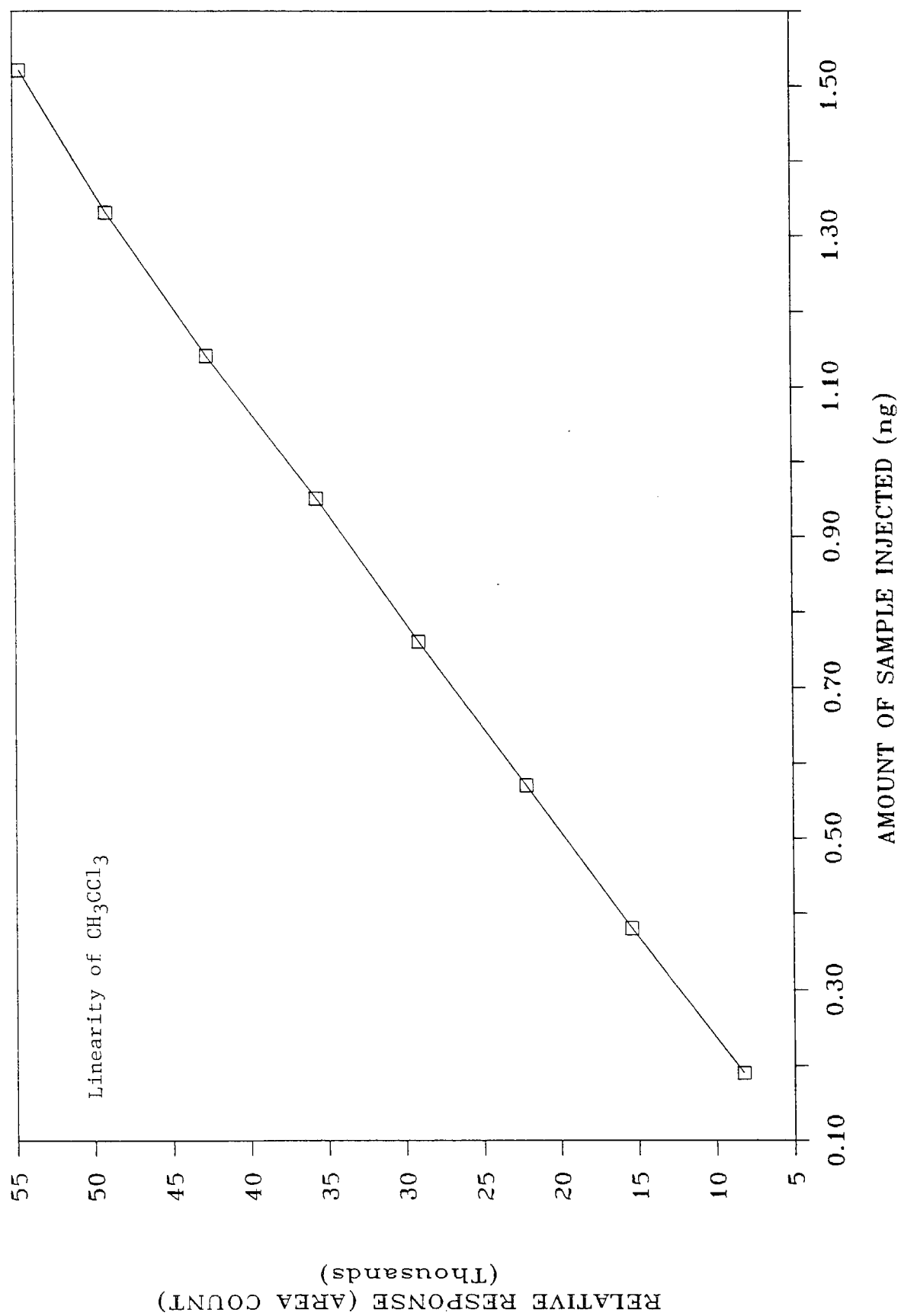


Figure 6

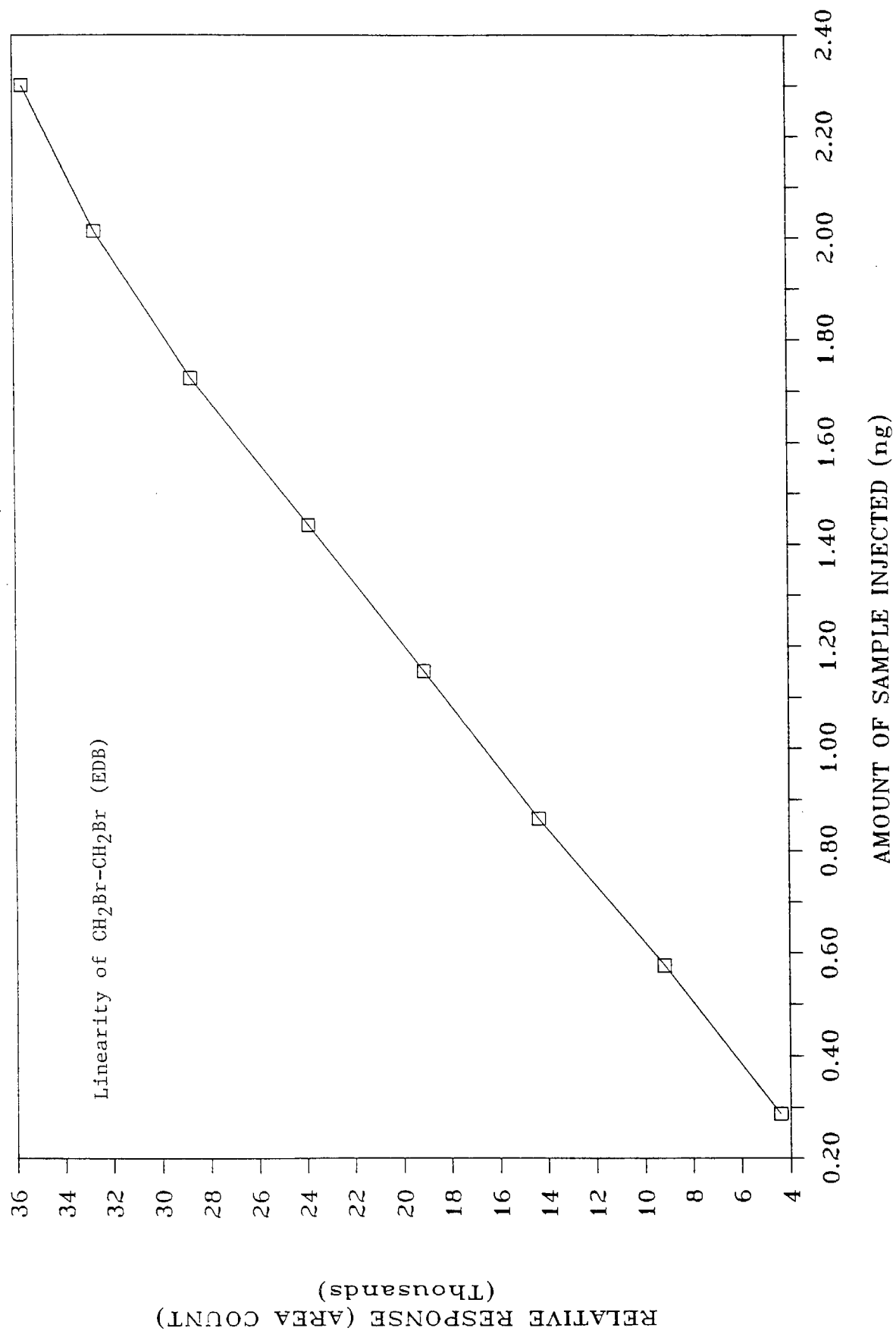




Figure 7

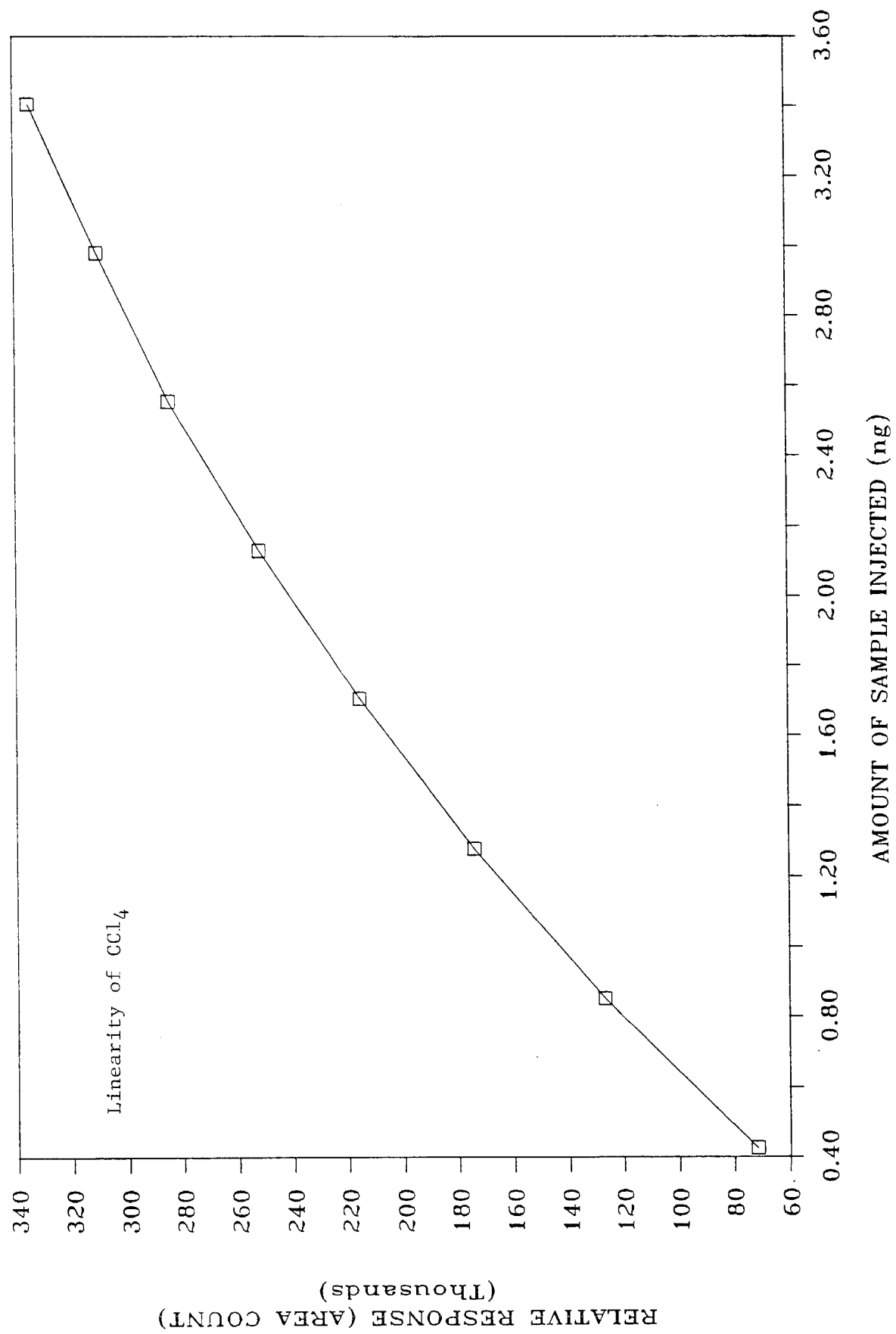


Figure 8

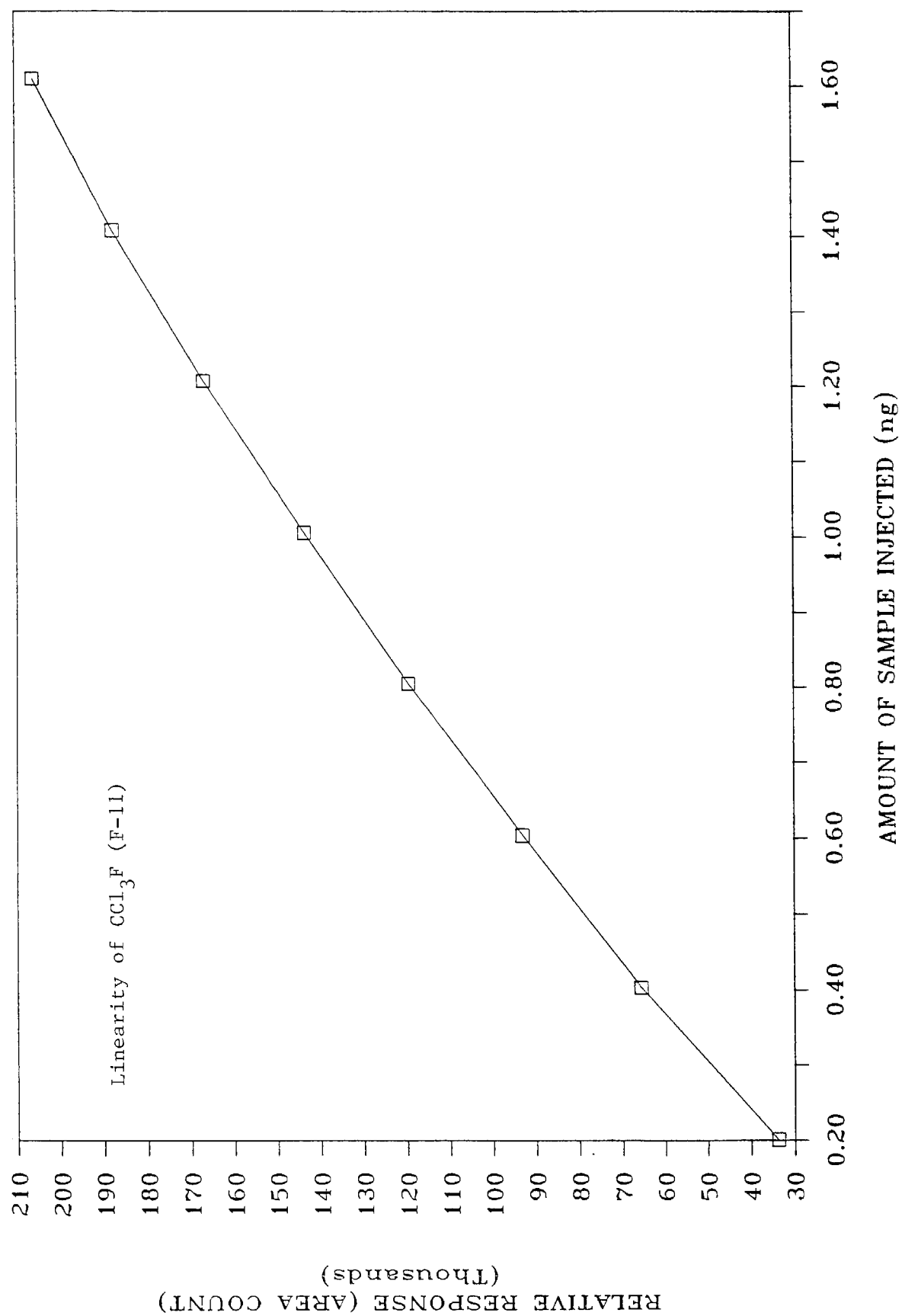


Figure 9

